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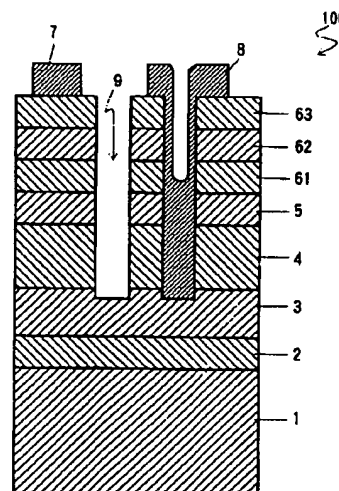
## Remarks:

This application was filed on 13 - 11 - 2000 as a divisional application to the application mentioned under INID code 62.

(54) **Light-emitting semiconductor device using group III nitride compound**

(57) A light-emitting semiconductor device (100) having an improved metal contact to semiconductor connection that lowers the device drive voltage includes a sapphire substrate (1), an 500 Å thick AlN buffer layer (2), a 2.0 μm thick silicon (Si) doped GaN n<sup>+</sup>-layer (3) of high carrier (n-type) concentration with an electron concentration of  $2 \times 10^{18}/\text{cm}^3$ , a 2.0 μm thick Si-doped (Al<sub>x2</sub>Ga<sub>1-x2</sub>)<sub>2</sub>In<sub>1-y2</sub>N n<sup>+</sup>-layer (4) of high carrier (n-type) concentration with an electron concentration of  $2 \times 10^{18}/\text{cm}^3$ , a 0.5 μm thick magnesium (Mg), zinc (Zn), and Si-doped (Al<sub>x1</sub>Ga<sub>1-x1</sub>)<sub>y1</sub>In<sub>1-y1</sub>N emission layer (5), and a 1.0 μm thick Mg-doped (Al<sub>x2</sub>Ga<sub>1-x2</sub>)<sub>2</sub>In<sub>1-y2</sub>N p-layer (61), a 0.2 μm thick Mg-doped GaN second contact layer (62) with  $5 \times 10^{17}/\text{cm}^3$  hole concentration and  $1 \times 10^{20}/\text{cm}^3$  Mg concentration, and a 500 Å thick Mg-doped GaN first contact layer (63) with a hole concentration of  $2 \times 10^{17}/\text{cm}^3$  and with a Mg concentration of  $2 \times 10^{20}/\text{cm}^3$ . Nickel electrodes (7, 8) are connected to the p-layer (61) and the n<sup>+</sup>-layer (4), respectively.

FIG. 1



**Description**

wherein the contact layer is doped with an acceptor impurity more heavily than the p-layer.

**BACKGROUND OF THE INVENTION****Field of the invention**

**[0001]** The present invention relates to a light-emitting semiconductor device that uses a Group III nitride compound, and, more particularly, to a LED having an improved metal-to-semiconductor contact.

**Description of the Prior Art**

**[0002]** It has been known that an aluminum gallium indium nitride (AlGaInN) compound semiconductor may be used to obtain a light-emitting diode (LED) which emits blue light. This semiconductor device is useful because of its high luminous efficiency resulting from direct electron transition and because of its ability to emit blue light, which is one of the three primary colors.

**[0003]** Irradiating an electron beam into and heat treatment of a magnesium (Mg) doped i-layer alters it to exhibit p-type conduction. As a result, a LED with a double hetero p-n junction structure made of an aluminum gallium nitride (AlGaN) p layer, a zinc (Zn) doped indium gallium nitride (InGaN) emission layer, and an AlGaN n-layer is preferable when compared to a conventional LED of metal insulator semiconductor (MIS) structure which includes an n-layer and a semi-insulating i-layer.

**[0004]** The conventional LED with a double hetero p-n junction structure utilizes a GaN layer doped with Mg on order of  $10^{19}/\text{cm}^3$  as a contact layer for the p-layer. The carrier concentration of the p-layer is high and a  $7 \times 10^{17}/\text{cm}^3$  hole injection efficiency. The inventors of the present invention found for the first time that the GaN contact layer prevents a decrease in the driving voltage because of the Schottky barrier at the metal semiconductor electrode interface.

**SUMMARY OF THE INVENTION**

**[0005]** It is, therefore, an object of the present invention to lower the driving voltage of a LED without diminishing the hole injection efficiency by forming a new LED structure which provides excellent ohmic contact to the electrodes of the device.

**[0006]** According to the first aspect of the invention, there is provided a light-emitting semiconductor device constituted by:

- an n-layer with n-type conduction of Group III nitride compound semiconductor satisfying the formula  $\text{Al}_x\text{Ga}_y\text{In}_{1-x-y}\text{N}$ , inclusive of  $x=0$ ,  $y=0$ , and  $x=y=0$ ;
- a p-layer with p-type conduction of Group III nitride compound semiconductor satisfying the formula  $\text{Al}_x\text{Ga}_y\text{In}_{1-x-y}\text{N}$ , inclusive of  $x=0$ ,  $y=0$ , and  $x=y=0$ ;
- a contact layer for the p-layer directly contacting a metal electrode; and

**[0007]** According to the second aspect of the invention, Mg is used as an acceptor.

**[0008]** According to the third aspect of the invention, the contact layer is doped with magnesium (Mg) in the  $1 \times 10^{20}/\text{cm}^3$  to  $1 \times 10^{21}/\text{cm}^3$  range exhibiting p-type conduction.

**[0009]** According to the fourth aspect of the invention, the contact layer for the p-layer directly contacts the metal electrode and is doped with magnesium (Mg) in the  $1 \times 10^{20}/\text{cm}^3$  to  $1 \times 10^{21}/\text{cm}^3$  range exhibiting p-type conduction.

**[0010]** According to the fifth aspect of the invention, the contact layer has a double p-layer structure constituted by a first contact layer being doped with magnesium (Mg) in the  $1 \times 10^{20}/\text{cm}^3$  to  $1 \times 10^{21}/\text{cm}^3$  range, exhibiting p-type conduction and directly contacting the metal electrodes, and a second contact layer being doped with magnesium (Mg) more lightly than the first contact layer in the  $1 \times 10^{19}/\text{cm}^3$  to  $5 \times 10^{20}/\text{cm}^3$  range.

**[0011]** According to the sixth aspect of the invention, the contact layer is doped with magnesium (Mg) in the  $1 \times 10^{20}/\text{cm}^3$  to  $1 \times 10^{21}/\text{cm}^3$  range exhibiting p-type conduction and directly contacts the metal electrodes, and the p-layer contacting the contact layer is doped with magnesium (Mg) more lightly than the contact layer in the  $1 \times 10^{19}/\text{cm}^3$  to  $5 \times 10^{20}/\text{cm}^3$  range.

**[0012]** According to the seventh aspect of the invention, the contact layer is made of gallium nitride (GaN) and the metal electrode is made of nickel (Ni) or an alloy of Ni.

**[0013]** As described above, doping an acceptor impurity more heavily into the contact layer for the p-layer directly contacting the metal electrode than the p-layer provides better ohmic characteristic to the metal electrode. As a result, the driving voltage of the device can be lowered to 4 V.

**[0014]** When the acceptor impurity is Mg, its preferable concentration is in the  $1 \times 10^{20}/\text{cm}^3$  to  $1 \times 10^{21}/\text{cm}^3$  range. A Mg-doped first contact layer in that range which is exhibiting p-type conduction and directly contacting a metal electrode can improve ohmic characteristic but lowers the hole concentration in the layer. In order to prevent decreased hole concentration, another layer is provided just below the Mg-doped first contact layer as a second contact layer or a p-layer. The second contact layer or the p-layer is doped with Mg more lightly than the Mg-doped first contact layer in the  $1 \times 10^{19}/\text{cm}^3$  to  $5 \times 10^{20}/\text{cm}^3$  range. As a result, the hole concentration of the second contact layer or the p-layer is increased preventing a luminous efficiency decrease.

**[0015]** Other objects, features, and characteristics of the present invention will become apparent upon consideration of the following description in the appended claims with reference to the accompanying drawings, all of which form a part of the specification, and wherein

referenced numerals designate corresponding parts in the various figures.

#### BRIEF DESCRIPTION OF THE DRAWING

[0016] In the accompanying drawings:

FIG. 1 is a diagram showing the structure of the LED in Example 1;

FIGS. 2 through 7 are sectional views illustrating successive steps of producing the LED in Example 1;

FIG. 8 is a diagram showing the structure of the LED in Example 2;

FIGS. 9 and 10 are diagrams showing the structure of the LED in Example 3;

FIG. 11 is a graph showing the dependence of driving voltage on Mg concentration doped into the first contact layer; and

FIG. 12 is a graph showing the dependence of hole concentration of the second contact layer or the p-layer on Mg concentration doped into the second contact layer or the p-layer.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0017] The invention will be more fully understood by reference to the following examples.

##### Example 1

[0018] FIG. 1 shows a LED 100 embodied in Example 1. It has a sapphire ( $\text{Al}_2\text{O}_3$ ) substrate 1 upon which the following seven layers are consecutively formed: an AlN buffer layer 2; a silicon (Si) doped GaN  $n^+$ -layer 3 of high carrier (n-type) concentration; a Si-doped ( $\text{Al}_{x_2}\text{Ga}_{1-x_2}$ ) $_{y_2}\text{In}_{1-y_2}\text{N}$   $n^+$ -layer 4 of high carrier (n-type) concentration; magnesium (Mg), a cadmium (Cd), and Si-doped ( $\text{Al}_{x_1}\text{Ga}_{1-x_1}$ ) $_{y_1}\text{In}_{1-y_1}\text{N}$  p-type emission layer 5; a Mg-doped ( $\text{Al}_{x_2}\text{Ga}_{1-x_2}$ ) $_{y_2}\text{In}_{1-y_2}\text{N}$  p-layer 61; a Mg-doped second GaN contact layer 62; and a Mg-doped first GaN contact layer 63. The AlN layer 2 has a 500 Å thickness. The GaN  $n^+$ -layer 3 is about 2.0  $\mu\text{m}$  in thickness and has a  $2 \times 10^{18}/\text{cm}^3$  electron concentration. The  $n^+$ -layer 4 is about 2.0  $\mu\text{m}$  in thickness and has a  $2 \times 10^{18}/\text{cm}^3$  electron concentration. The emission layer 5 has about a 0.5  $\mu\text{m}$  thickness. The p-layer 61 has about 1.0  $\mu\text{m}$  thickness, a  $5 \times 10^{17}/\text{cm}^3$  hole concentration, and a  $1 \times 10^{20}/\text{cm}^3$  Mg concentration. The second contact layer 62 has about 0.2  $\mu\text{m}$  thickness, a  $5 \times 10^{17}/\text{cm}^3$  hole concentration, and a  $1 \times 10^{20}/\text{cm}^3$  Mg concentration. The first contact layer 63 has a 500 Å thickness, a  $2 \times 10^{17}/\text{cm}^3$  hole concentration, and a  $2 \times 10^{20}/\text{cm}^3$  Mg concentration. Nickel electrodes 7 and 8 are connected to the first contact layer 63 and the  $n^+$ -layer 4, respectively. The electrodes 7 and 8 are electrically insulated from one another by a groove 9.

[0019] The LED 100 is produced by gaseous phase epitaxial growth, called metal organic vapor phase epitaxy referred to as MOVPE hereinafter.

[0020] The gases employed in this process are ammonia ( $\text{NH}_3$ ), a carrier gas ( $\text{H}_2$  or  $\text{N}_2$ ), trimethyl gallium ( $\text{Ga}(\text{CH}_3)_3$ ) (TMG hereinafter), trimethyl aluminum ( $\text{Al}(\text{CH}_3)_3$ ) (TMA hereinafter), trimethyl indium ( $\text{In}(\text{CH}_3)_3$ ) (TMI hereinafter), dimethylcadmium ( $(\text{Cd}(\text{CH}_3)_2)$  (DMCd hereinafter), silane ( $\text{SiH}_4$ ), and bis-cyclopentadienyl magnesium ( $\text{Mg}(\text{C}_5\text{H}_5)_2$ ) ( $\text{CP}_2\text{Mg}$  hereinafter).

[0021] The single crystalline sapphire substrate 1, whose main surface 'a' was cleaned by an organic washing solvent and heat treatment, was placed on a susceptor in a reaction chamber for the MOVPE treatment. Then the sapphires substrate 1 was etched at 1100 °C by a vapor of  $\text{H}_2$  fed into the chamber at a flow rate of 2 liter/min. under normal pressure for a period of 5 min.

[0022] On the etched sapphire substrate 1, a 500 Å thick AlN buffer layer 2 was formed on the surface 'a' under conditions of lowering the temperature in the chamber to 400 °C, keeping the temperature constant, and supplying  $\text{H}_2$  at a flow rate of 20 liter/min.,  $\text{NH}_3$  at 10 liter/min., and TMA at  $1.8 \times 10^{-5}$  mol/min. for a period of about 90 sec. On the buffer layer 2, about a 2.0  $\mu\text{m}$  thick Si-doped GaN  $n^+$ -layer 3 of high carrier concentration with an electron concentration of about  $2 \times 10^{18}/\text{cm}^3$  was formed under conditions of keeping the temperature of the sapphire substrate 1 at 1150 °C and supplying  $\text{H}_2$  at a flow rate of 20 liter/min.,  $\text{NH}_3$  at 10 liter/min., TMG at  $1.7 \times 10^{-4}$  mol/min., and diluted silane to 0.86 ppm by  $\text{H}_2$  at 200 ml/min. for 30 minutes, respectively.

[0023] The following manufacturing process provides for an emission layer 5 as an active layer, an  $n^+$ -layer 4 of high carrier concentration and a p-layer 61 as clad layers; the LED 100 is designed to emit at a 430 nm wavelength peak in the luminous spectrum and has luminous centers of Cd and Si.

[0024] On the  $n^+$ -layer 3, about a 2.0  $\mu\text{m}$  thick Si-doped ( $\text{Al}_{0.47}\text{Ga}_{0.53}$ ) $_{0.9}\text{In}_{0.1}\text{N}$   $n^+$ -layer 4 of high carrier concentration with an electron concentration of  $1 \times 10^{18}/\text{cm}^3$  was formed under conditions of keeping the temperature of the sapphire substrate 1 at 850 °C and supplying  $\text{N}_2$  or  $\text{H}_2$  at a flow rate of 10 liter/min.,  $\text{NH}_3$  at 10 liter/min., TMG at  $1.12 \times 10^{-4}$  mol/min., TMA at  $0.47 \times 10^{-4}$  mol/min., TMI at  $0.1 \times 10^{-4}$  mol/min., and diluted silane to 0.86 ppm by  $\text{H}_2$  at  $10 \times 10^{-9}$  mol/min. for 60 min.

[0025] On the  $n^+$ -layer 4, about a 0.5  $\mu\text{m}$  thick Mg-, Cd-, and Si-doped ( $\text{Al}_{0.3}\text{Ga}_{0.7}$ ) $_{0.94}\text{In}_{0.06}\text{N}$  emission layer 5 was formed under conditions of keeping the temperature of the sapphire substrate 1 at 850 °C and supplying  $\text{N}_2$  or  $\text{H}_2$  at a flow rate of 20 liter/min.,  $\text{NH}_3$  at 10 liter/min., TMG at  $1.53 \times 10^{-4}$  mol/min., TMA at  $0.47 \times 10^{-4}$  mol/min., TMI  $0.02 \times 10^{-4}$  mol/min.,  $\text{CP}_2\text{Mg}$  at  $2 \times 10^{-4}$  mol/min., DMCd at  $2 \times 10^{-7}$  mol/min., and diluted

silane to 0.86 ppm by  $H_2$  at  $10 \times 10^{-9}$  mol/min. for 60 min. At this stage, the layer 5 exhibited high resistivity. The impurity concentrations of Mg, Cd, and Si doped into the emission layer 5 were  $1 \times 10^{19}/cm^3$ ,  $5 \times 10^{18}/cm^3$ , and  $1 \times 10^{18}/cm^3$ , respectively.

[0026] On the emission layer 5, about a  $1.0 \mu m$  thick Mg-doped  $(Al_{0.47}Ga_{0.53})_{0.9}In_{0.1}N$  p-layer 61 was formed under conditions of keeping the temperature of the sapphire substrate 1 at  $1100^\circ C$  and supplying  $N_2$  or  $H_2$  at a flow rate of 20 liter/min.,  $NH_3$  at 10 liter/min., TMG at  $1.12 \times 10^{-4}$  mol/min., TMA at  $0.47 \times 10^{-4}$  mol/min., TMI at  $0.1 \times 10^{-4}$  mol/min., and  $CP_2Mg$  at  $2 \times 10^{-4}$  mol/min. for 120 min. Resistivity of the p-layer 61 was  $10^8 \Omega \cdot cm$  or more exhibiting insulative characteristics. The impurity concentration of Mg doped into the p-layer 61 was  $1 \times 10^{20}/cm^3$ .

[0027] On the p-layer 61, about a  $0.2 \mu m$  thick Mg-doped GaN second contact layer 62 was formed under conditions of keeping the temperature of the sapphire substrate 1 at  $850^\circ C$  and supplying  $N_2$  or  $H_2$  at a flow rate of 20 liter/min.,  $NH_3$  at 10 liter/min., TMG at  $1.12 \times 10^{-4}$  mol/min., and  $CP_2Mg$  at  $2 \times 10^{-4}$  mol/min. for 30 min. Resistivity of the second contact layer 62 was  $10^8 \Omega \cdot cm$  or more exhibiting insulative characteristics. The impurity concentration of Mg doped into the GaN layer 62 was  $1 \times 10^{20}/cm^3$ .

[0028] On the GaN layer 62, about a  $500 \text{ \AA}$  thick Mg-doped GaN first contact layer 63 was formed under conditions of keeping the temperature of the sapphire substrate 1 at  $850^\circ C$  and supplying  $N_2$  or  $H_2$  at a flow rate of 20 liter/min.,  $NH_3$  at 10 liter/min., TMG at  $1.12 \times 10^{-4}$  mol/min., and  $CP_2Mg$  at  $4 \times 10^{-4}$  mol/min. for 10 min. Resistivity of the first contact layer 63 was  $10^8 \Omega \cdot cm$  or more exhibiting insulative characteristics. The impurity concentration of Mg doped into the GaN layer 63 was  $2 \times 10^{20}/cm^3$ .

[0029] Then, electron rays were uniformly irradiated into the first contact layer 63, the second contact layer 62, the p-layer 61, and the emission layer 5 using a reflective electron beam diffraction device. The irradiation conditions were set at 10 KV for the accelerating voltage,  $1 \mu A$  for the sample current, 0.2 mm/sec. for the speed of the beam scanning,  $60 \mu m \phi$  for the beam aperture, and at  $5.0 \times 10^{-5}$  Torr vacuum. This irradiation changed the insulative first contact layer 63, second contact layer 62, p-layer 61, and emission layer 5 into a p-type conductive semiconductor with a hole concentration of  $2 \times 10^{17}/cm^3$ ,  $5 \times 10^{17}/cm^3$ ,  $5 \times 10^{17}/cm^3$ , and  $5 \times 10^{17}/cm^3$  and a resistivity of  $2 \Omega \cdot cm$ ,  $0.8 \Omega \cdot cm$ ,  $0.8 \Omega \cdot cm$ , and  $0.8 \Omega \cdot cm$ , respectively. Thereby, a wafer with multi-structural layers was obtained as shown in FIG. 2.

[0030] FIGS. 3 to 7 show sectional views of the formations of an individual device on the wafer. In actual practice and in accordance with industry custom, a wafer with a large number of elements thereon is treated by the following process and divided or diced into individual devices.

[0031] A  $2000 \text{ \AA}$  thick  $SiO_2$  layer 11 was formed on the first contact layer 63 by sputtering. Then, the layer 11 was coated with a photoresist layer 12. Two selected parts or areas of the photoresist layer 12, named A and B, were removed by photolithography as shown in FIG. 3. The part or area A is an electrode-forming aperture which corresponds to a place where a hole 15, shown in FIG. 5, is formed extending to and into the  $n^+$ -layer 4 of high carrier concentration. The part or area B corresponds to a place where a trench-like isolation groove 9, shown in FIGS. 5 and 6, is formed for insulating or electrically insulating the part or area A from an electrode in contact with the p-layer 61.

[0032] As shown in FIG. 4, two parts of the  $SiO_2$  layer 11 which were not covered with the photoresist layer 12 were etched off by an etching liquid such as hydrofluoric acid. Then, the exposed part of the successive layers from the surface of the device, the first contact layer 63 to the emission layer 5, and the upper part of the  $n^+$ -layer 4 of high carrier concentration, were removed by dry etching, or supplying a high-frequency power density of  $0.44 W/cm^2$  and  $BCl_3$  gas of 10 ml/min. at a vacuum degree of 0.04 Torr as shown in FIG. 5. After that, dry etching with argon (Ar) was carried out on the device. Consequently, a hole 15 for forming an electrode extending into the  $n^+$ -layer 4 of high carrier concentration and a trench-like groove 9 for insulation purposes are formed.

[0033] The  $SiO_2$  layer 11 remaining on the GaN p-layer 63 was removed by hydrofluoric acid as shown in FIG. 6. A nickel (Ni) layer 13 was laminated on the entire surface of the device by vapor deposition (FIG. 7). Thus, the so-formed Ni layer 13 in the hole 15 is in electrical contact with the  $n^+$ -layer 4 of high carrier concentration. A photoresist 14 was deposited on the Ni layer 13. The photoresist 14 was then selectively etched off by photolithography leaving patterns of configuration (FIG. 7) for the to-be-formed electrodes connected to the  $n^+$ -layer 4 of high carrier concentration and the p-layer 63, respectively.

[0034] Using the photoresist 14 as a mask, the exposed part or area of the Ni layer 13 from the photoresist 14 was etched off by an etching liquid such as nitric acid. At this time, the nickel layer 13 laminated in the groove 9 was also removed completely. Then, the photoresist layer 14 was removed by a photoresist removal liquid such as acetone. Two electrodes were formed, the electrode 8 for the  $n^+$ -layer 4 of high carrier concentration and the electrode 7 for the p-layer 63. The trench-like groove 9 insulates the electrodes 7 and 8 from one another. A wafer treated with the above-mentioned process was divided or diced into each chip or element which thus constituted a gallium nitride compound LED with a p-p-n junction structure as shown in FIG. 1.

[0035] The obtained LED 100 was found to have a luminous intensity of 1 cd and a wavelength of 430 nm at a driving current of 20 mA.

[0036] Preferable impurity concentrations of Si and

Cd doped into the emission layer 5 are in the  $1 \times 10^{17}/\text{cm}^3$  to  $1 \times 10^{20}/\text{cm}^3$  range, respectively, for higher luminous intensity. Further, the preferable concentration of Si is half to one-tenth as much as that of Cd.

**[0037]** In this embodiment, the LED 100 has a double-hetero junction structure sandwiching the emission layer 5 by the p-layer 61 and the n<sup>+</sup>-layer 4 which have wider band gaps than that of the emission layer 5. The composition ratio of Al, Ga, and In of the three layers are designed to match the lattice constant of the GaN n<sup>+</sup>-layer 3 of high carrier concentration.

#### Example 2

**[0038]** FIG. 8 shows a LED 200 in Example 2. The difference between the LED 100 in Example 1 and the LED 200 resides in the impurity doped into the emission layer 5. In Example 1, Mg, Cd, and Si are doped into the emission layer 5, and, in Example 2, Mg, Zn, and Si are doped.

**[0039]** The sapphire substrate 1 to the n<sup>+</sup>-layer 3 were prepared by the same methods that described in Example 1. On the n<sup>+</sup>-layer 3, about a 0.5  $\mu\text{m}$  thick Si-doped ( $\text{Al}_{0.3}\text{Ga}_{0.7}\text{In}_{0.06}\text{N}$ ) n<sup>+</sup>-layer 4 of high carrier concentration with an electron concentration of  $2 \times 10^{19}/\text{cm}^3$  was formed under conditions of keeping the temperature of the sapphire substrate 1 at 800 °C and supplying N<sub>2</sub> or H<sub>2</sub> at a flow rate of 20 liter/min.; NH<sub>3</sub> at 10 liter/min., TMG at  $1.12 \times 10^{-4}$  mol/min., TMA at  $0.47 \times 10^{-4}$  mol/min., TMI at  $0.1 \times 10^{-4}$  mol/min., and diluted silane to 0.86 ppm by H<sub>2</sub> at  $10 \times 10^{-9}$  mol/min. for 60 min.

**[0040]** On the n<sup>+</sup>-layer 4, about a 0.5  $\mu\text{m}$  thick Mg-, Si-, and Zn-doped ( $\text{Al}_{0.09}\text{Ga}_{0.91}\text{In}_{0.01}\text{N}$ ) emission layer 5 was formed under conditions of keeping the temperature of the sapphire substrate 1 at 1150 °C and supplying N<sub>2</sub> at a flow rate of 20 liter/min., NH<sub>3</sub> at 10 liter/min., TMG at  $1.53 \times 10^{-4}$  mol/min., TMA at  $0.47 \times 10^{-4}$  mol/min., TMI  $0.02 \times 10^{-4}$  mol/min., CP<sub>2</sub>Mg at  $2 \times 10^{-4}$  mol/min., DEZ at  $2 \times 10^{-4}$  mol/min., and diluted silane to 0.86 ppm by H<sub>2</sub> at  $10 \times 10^{-9}$  mol/min. for 60 min. The impurity concentration of Mg, Zn, and Si doped into the emission layer 5 was  $1 \times 10^{19}/\text{cm}^3$ ,  $2 \times 10^{18}/\text{cm}^3$ , and  $1 \times 10^{18}/\text{cm}^3$ , respectively.

**[0041]** On the emission layer 5, about a 1.0  $\mu\text{m}$  thick Mg-doped ( $\text{Al}_{0.3}\text{Ga}_{0.7}\text{In}_{0.06}\text{N}$ ) p-layer 61 was formed under conditions of keeping the temperature of the sapphire substrate 1 at 1100 °C and supplying N<sub>2</sub> at a flow rate of 20 liter/min., NH<sub>3</sub> at 10 liter/min., TMG at  $1.12 \times 10^{-4}$  mol/min., TMA at  $0.47 \times 10^{-4}$  mol/min., TMI at  $0.1 \times 10^{-4}$  mol/min., and CP<sub>2</sub>Mg at  $2 \times 10^{-4}$  mol/min. for 120 min. Resistivity of the p-layer 61 was  $10^8 \Omega \cdot \text{cm}$  or 30 more exhibiting insulative characteristics. The impurity concentration of the Mg doped into the p-layer 61 was  $1 \times 10^{20}/\text{cm}^3$ .

**[0042]** On the p-layer 61, about a 2.0  $\mu\text{m}$  thick Mg-doped GaN second contact layer 62 was formed under conditions of keeping the temperature of the sapphire

substrate 1 at 850 °C and supplying N<sub>2</sub> or H<sub>2</sub> at a flow rate of 20 liter/min., NH<sub>3</sub> at 10 liter/min., TMG at  $1.12 \times 10^{-4}$  mol/min., and CP<sub>2</sub>Mg at  $2 \times 10^{-4}$  mol/min. for 30 min. Resistivity of the p-layer 62 was  $10^8 \Omega \cdot \text{cm}$  or more exhibiting insulative characteristics. The impurity concentration of the Mg doped into the second contact layer 62 was  $1 \times 10^{20}/\text{cm}^3$ .

**[0043]** On the layer 62, about a 500 Å thick Mg-doped GaN first contact layer 63 was formed under conditions of keeping the temperature of the sapphire substrate 1 at 850 °C and supplying N<sub>2</sub> or H<sub>2</sub> at a flow rate of 20 liter/min., NH<sub>3</sub> at 10 liter/min., TMG at  $1.12 \times 10^{-4}$  mol/min., and CP<sub>2</sub>Mg at  $4 \times 10^{-4}$  mol/min. for 10 min. Resistivity of the first contact layer 63 was  $10^8 \Omega \cdot \text{cm}$  or more exhibiting insulative characteristics. The impurity concentration of the Mg doped into the GaN layer 63 was  $2 \times 10^{20}/\text{cm}^3$ .

**[0044]** Then, electron rays were uniformly irradiated into the first contact layer 63, the second contact layer 62, the p-layer 61, and the emission layer 5 using a reflective electron beam diffraction device. The irradiation conditions were the same that described in Example 1. This irradiation changed each of the insulative first contact layer 63, second contact layer 62, p-layer 61, and emission layer 5 into a p-type conductive semiconductor. The obtained LED 200 was found to have a luminous intensity of 1 cd and a wavelength of 430 nm at a driving voltage of 4V.

#### Example 3

**[0045]** FIGS. 9 and 10 show a LED 300 in Example 3. The difference between the LED 200 in Example 2 and the LED 300 resides in the n<sup>+</sup>-layer 4, the emission layer 5, and the p-layer 61. In Example 3, the n<sup>+</sup>-layer 4 of high carrier concentration is constituted by Si-doped  $\text{Al}_{x2}\text{Ga}_{1-x2}\text{N}$ , the emission layer 5 is by Mg-, Zn-, and Si-doped  $\text{Ga}_y\text{In}_{1-y}\text{N}$ , and the p-layer 61 is by Mg-doped  $\text{Al}_{x1}\text{Ga}_{1-x1}\text{N}$ . The composition ratio of x1, y, and x2 of the three layers are designed to form a double-hetero junction structure sandwiching the emission layer 5 by the n<sup>+</sup>-layer 4 and the p-layer 61 which have a wider band gap than that of the emission layer 5. Other layers such as the first contact layer 62 and the second contact layer 63 are as same as those in Examples 1 and 2.

**[0046]** As shown in FIG. 10, the LED 300 has a sapphire ( $\text{Al}_2\text{O}_3$ ) substrate 1 upon which the following seven layers are consecutively formed: an AlN buffer layer 2; a Si-doped GaN n<sup>+</sup>-layer 3 of high carrier (n-type) concentration; a Si-doped  $\text{Al}_{0.1}\text{Ga}_{0.9}\text{N}$  n<sup>+</sup>-layer 4 of high carrier (n-type) concentration; Mg-, Zn-, and Si-doped  $\text{Ga}_{0.94}\text{In}_{0.06}\text{N}$  p-type emission layer 5; a Mg-doped  $\text{Al}_{0.1}\text{Ga}_{0.9}\text{N}$  p-layer 61; a Mg-doped GaN second contact layer 62; and a Mg-doped GaN first contact layer 63. The AlN layer 2 has a 500 Å thickness. The GaN n<sup>+</sup>-layer 3 is about 2.0  $\mu\text{m}$  in thickness and has a  $2 \times 10^{18}/\text{cm}^3$  electron concentration. The n<sup>+</sup>-layer 4 is about 4.0  $\mu\text{m}$  in thickness and has a  $2 \times 10^{18}/\text{cm}^3$  elec-

tron concentration. The emission layer 5 has about a 0.5  $\mu\text{m}$  thickness. The p-layer 61 has about 0.5  $\mu\text{m}$  thickness, a  $5 \times 10^{17}/\text{cm}^3$  hole concentration, and a  $1 \times 10^{19}/\text{cm}^3$  Mg concentration. The second contact layer 62 has about 0.2  $\mu\text{m}$  thickness, a  $5 \times 10^{17}/\text{cm}^3$  hole concentration, and a  $1 \times 10^{20}/\text{cm}^3$  Mg concentration. The first contact layer 63 has a 500 Å thickness, a  $2 \times 10^{17}/\text{cm}^3$  hole concentration, and a  $2 \times 10^{20}/\text{cm}^3$  Mg concentration. Nickel electrodes 7 and 8 are connected to the first contact layer 63 and the  $n^+$ -layer 4, respectively. They are electrically insulated by a groove 9.

**[0047]** Manufacturing process of the LED 300 is described hereinafter. The sapphire substrate 1, the AlN buffer layer 2, the  $n^+$ -layer 3 were prepared by the same way that described in Example 1. On the  $n^+$ -layer 3, about a 4.0  $\mu\text{m}$  thick Si-doped  $\text{Al}_{0.1}\text{Ga}_{0.9}\text{N}$   $n^+$ -layer 4 of high carrier concentration with an electron concentration of  $2 \times 10^{18}/\text{cm}^3$  was formed under conditions of keeping the temperature of the sapphire substrate 1 at 1150 °C and supplying  $\text{N}_2$  or  $\text{H}_2$  at a flow rate of 20 liter/min.,  $\text{NH}_3$  at 10 liter/min., TMG at  $1.12 \times 10^{-4}$  mol/min., TMA at  $0.47 \times 10^{-4}$  mol/min., and diluted silane to 0.86 ppm by  $\text{H}_2$  at  $10 \times 10^{-9}$  mol/min. for 60 min.

**[0048]** The following manufacturing process provides for an emission layer 5 as an active layer, a p-layer 61, a second contact layer 62, and a first contact layer 63 as clad layers; the LED 300 is designed to emit at a 450 nm wavelength peak in the luminous spectrum and has luminous centers of Zn and Si.

**[0049]** On the  $n^+$ -layer 4, about a 0.5  $\mu\text{m}$  thick Mg-, Si-, and Zn-doped  $\text{Ga}_{0.94}\text{In}_{0.06}\text{N}$  emission layer 5 was formed under conditions of keeping the temperature of the sapphire substrate 1 at 850 °C and supplying  $\text{N}_2$  at a flow rate of 20 liter/min.,  $\text{NH}_3$  at 10 liter/min., TMG at  $1.53 \times 10^{-4}$  mol/min., TMI  $0.02 \times 10^{-4}$  mol/min.,  $\text{CP}_2\text{Mg}$  at  $2 \times 10^{-4}$  mol/min., DEZ at  $2 \times 10^{-7}$  mol/min., and diluted silane to 0.86 ppm by  $\text{H}_2$  at  $10 \times 10^{-9}$  mol/min. for 60 min. At this stage, the emission layer 5 exhibits insulative characteristics.

**[0050]** On the emission layer 5, about a 0.5  $\mu\text{m}$  thick Mg-doped  $\text{Al}_{0.1}\text{Ga}_{0.9}\text{N}$  p-layer 61 was formed under conditions of keeping the temperature of the sapphire substrate 1 at 850 °C and supplying  $\text{N}_2$  at a flow rate of 20 liter/min.,  $\text{NH}_3$  at 10 liter/min., TMG at  $1.12 \times 10^{-4}$  mol/min., TMA at  $0.47 \times 10^{-4}$  mol/min., and  $\text{CP}_2\text{Mg}$  at  $2 \times 10^{-7}$  mol/min. for 60 min. Resistivity of the p-layer 61 was  $10^8 \Omega \cdot \text{cm}$  or more exhibiting insulative characteristics. The impurity concentration of Mg doped into the p-layer 61 was  $1 \times 10^{19}/\text{cm}^3$ .

**[0051]** On the p-layer 61, about a 0.5  $\mu\text{m}$  thick Mg-doped GaN second contact layer 62 was formed under conditions of keeping the temperature of the sapphire substrate 1 at 850 °C and supplying  $\text{N}_2$  or  $\text{H}_2$  at a flow rate of 20 liter/min.,  $\text{NH}_3$  at 10 liter/min., TMG at  $1.12 \times 10^{-4}$  mol/min., and  $\text{CP}_2\text{Mg}$  at  $2 \times 10^{-4}$  mol/min. for 30 min. Resistivity of the p-layer 62 was  $10^8 \Omega \cdot \text{cm}$  or more exhibiting insulative characteristics. The impurity con-

centration of Mg doped into the GaN layer 62 was  $1 \times 10^{20}/\text{cm}^3$ .

**[0052]** On the second contact layer 62, about a 500 Å thick Mg-doped GaN first contact layer 63 was formed under conditions of keeping the temperature of the sapphire substrate 1 at 850 °C and supplying  $\text{N}_2$  or  $\text{H}_2$  at a flow rate of 20 liter/min.,  $\text{NH}_3$  at 10 liter/min., TMG at  $1.12 \times 10^{-4}$  mol/min., and  $\text{CP}_2\text{Mg}$  at  $4 \times 10^{-4}$  mol/min. for 10 min. The impurity concentration of Mg doped into the GaN layer 63 was  $2 \times 10^{20}/\text{cm}^3$ .

**[0053]** Then, electron rays were uniformly irradiated into the first contact layer 63, the second contact layer 62, the p-layer 61, and the emission layer 5 using a reflective electron beam diffraction device. The irradiation conditions were the same that described in Example 1. This irradiation changed the insulative first contact layer 63, second contact layer 62, p-layer 61, and emission layer 5 into a p-type conductive semiconductor with a hole concentration of  $2 \times 10^{17}/\text{cm}^3$ ,  $5 \times 10^{17}/\text{cm}^3$ , and  $5 \times 10^{17}/\text{cm}^3$ , and a resistivity of  $2 \Omega \cdot \text{cm}$ ,  $0.8 \Omega \cdot \text{cm}$ ,  $0.8 \Omega \cdot \text{cm}$ , and  $0.8 \Omega \cdot \text{cm}$ , respectively.

**[0054]** When the electrode area was  $6 \times 10^{-4} \text{cm}^2$ , the driving voltage was 4 V at a 20 mA current and the contact resistance was 30 to 40  $\Omega$ . When the electrode area was  $1.6 \times 10^{-3} \text{cm}^2$ , the driving voltage was 3.5 V at a 20 mA current and the contact resistance was 10 to 15  $\Omega$ .

**[0055]** FIG. 11 shows the dependence of the device driving voltage at a 20 mA electric current (ordinate) as a function of the Mg concentration doped into the first contact layer 63 (abscissa). The Mg concentration was altered from  $1 \times 10^{19}/\text{cm}^3$  to  $2 \times 10^{21}/\text{cm}^3$ . Accordingly, the driving voltage varied in the 11.2 V to 4.0 V range and contact resistance between the electrode 7 and the first contact layer 63 varied in the 250 to 30  $\Omega$  range. When the Mg concentration was  $2 \times 10^{20}/\text{cm}^3$ , the driving voltage exhibited the minimum 4.0 V and the contact resistance exhibited the minimum 30  $\Omega$ . When the Mg concentration was  $2 \times 10^{21}/\text{cm}^3$ , the driving voltage increased up to 5.0 V and the contact resistance increased to 70  $\Omega$ . Therefore, the desirable range of the Mg concentration doped into the first contact layer 63 was found to be in the  $1 \times 10^{20}/\text{cm}^3$  to  $1 \times 10^{21}/\text{cm}^3$  range in order to decrease the driving voltage to 5 V or lower.

**[0056]** FIG. 12 shows the dependence of the hole concentration of the second contact layer 62 or the p-layer 61 (ordinate) as a function of the Mg concentration (abscissa) doped into the second contact layer 62 or the p-layer 61. When the Mg concentration was increased to  $5 \times 10^{19}/\text{cm}^3$ , the hole concentration increased and saturated at the concentration of  $7 \times 10^{17}/\text{cm}^3$ . Further increase of Mg concentration decreased the hole concentration and the luminous efficiency. Therefore, it is preferable to dope Mg into the second contact layer 62 or the p-layer 61 in the  $1 \times 10^{19}/\text{cm}^3$  to  $5 \times 10^{20}/\text{cm}^3$  range and to keep the Mg concentration of the layer 62

or 61 lower than that of the first contact layer 63, because of the increased hole concentration of the second contact layer 62 and the improved luminous efficiency of the LED 300.

[0057] In Examples 1 to 3, the preferable concentration of Zn and Si doped into the emission layer 5 was found to range from  $1 \times 10^{17}/\text{cm}^3$  to  $1 \times 10^{20}/\text{cm}^3$  for improved luminous intensity, respectively. Further the preferable concentration of Zn and Si ranges from  $1 \times 10^{18}/\text{cm}^3$  to  $1 \times 10^{19}/\text{cm}^3$ , respectively. When the impurity concentration is  $1 \times 10^{18}/\text{cm}^3$  or lower, the doping impurities have little effect on luminous intensity. When the impurity concentration is  $1 \times 10^{19}/\text{cm}^3$  or higher, the crystallinity of the emission layer becomes poor. The preferable concentration of Si is one tenth to ten times as much as that of Zn. Further preferable concentration range of Si is one tenth to one as much as that of Zn.

[0058] In Examples 1 to 3, the contact layer had a double layer structure constituted by the first contact layer 63 heavily doped with Mg and the Mg-doped second contact layer 62 with a low Mg concentration relative to that of the first contact layer 63. Alternatively, only a Mg-doped contact layer which is doped higher than the emission layer 5 of p-type can be formed beneath the electrodes 7 and 8. GaN was utilized as the material of the contact layers 62 and 63. Alternatively, materials with the same composition ratio as the emission layer 5 of p-type can be used.

[0059] In Examples 1 to 3, Cd and Mg or Zn and Mg were employed as acceptor impurities and Si as a donor impurity. Alternatively, beryllium (Be) and mercury (Hg) can be used as an acceptor impurity and carbon (C), germanium (Ge), tin (Sn), lead (Pb), sulfur (S), selenium (Se), and tellurium (Te) can be used as a donor impurity.

[0060] Heat annealing, heat treatment in the atmosphere of  $\text{N}_2$  gases, or laser irradiation can be used as an alternative to electron irradiation to obtain p-type conduction.

[0061] While the invention has been described in connection with what are presently considered to be the most practical and preferred embodiments, it is to be understood that the invention is not to be limited to the disclosed embodiments, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

[0062] A light-emitting semiconductor device (100) having an improved metal contact to semiconductor connection that lowers the device drive voltage includes a sapphire substrate (1), an 500 Å thick AlN buffer layer (2), a 2.0 μm thick silicon (Si) doped GaN n<sup>+</sup>-layer (3) of high carrier (n-type) concentration with an electron concentration of  $2 \times 10^{18}/\text{cm}^3$ , a 2.0 μm thick Si-doped  $(\text{Al}_{x2}\text{Ga}_{1-x2})_{y2}\text{In}_{1-y2}\text{N}$  n<sup>+</sup>-layer (4) of high carrier (n-type) concentration with an electron concentration of  $2 \times 10^{18}/\text{cm}^3$ , a 0.5 μm thick magnesium (Mg), zinc (Zn), and Si-doped  $(\text{Al}_{x1}\text{Ga}_{1-x1})_{y1}\text{In}_{1-y1}\text{N}$  emission layer (5),

and a 1.0 μm thick Mg-doped  $(\text{Al}_{x2}\text{Ga}_{1-x2})_{y2}\text{In}_{1-y2}\text{N}$  p-layer (61), a 0.2 μm thick Mg-doped GaN second contact layer (62) with  $5 \times 10^{17}/\text{cm}^3$  hole concentration and  $1 \times 10^{20}/\text{cm}^3$  Mg concentration, and a 500 Å thick Mg-doped GaN first contact layer (63) with a hole concentration of  $2 \times 10^{17}/\text{cm}^3$  and with a Mg concentration of  $2 \times 10^{20}/\text{cm}^3$ . Nickel electrodes (7, 8) are connected to the p-layer (61) and the n<sup>+</sup>-layer (4), respectively.

## Claims

1. A light-emitting semiconductor device comprising:

a hetero junction structure including:

an n-layer having n-type conduction and a group III nitride compound semiconductor satisfying the formula  $\text{Al}_{x1}\text{Ga}_{y1}\text{In}_{1-x1-y1}\text{N}$ , where  $0 \leq x1 \leq 1$ ,  $0 \leq y1 \leq 1$ , and  $0 \leq x1 + y1 \leq 1$ ;

a p-layer having p-type conduction and a group III nitride compound satisfying the formula

$\text{Al}_{x3}\text{Ga}_{y3}\text{In}_{1-x3-y3}\text{N}$ , where  $0 \leq x3 \leq 1$ ,  $0 \leq y3 \leq 1$ , and  $0 \leq x3 + y3 \leq 1$ ; and

an emission layer of a group III nitride compound satisfying the formula  $\text{Al}_{x2}\text{Ga}_{y2}\text{In}_{1-x2-y2}\text{N}$ , where  $0 \leq x2 \leq 1$ ,  $0 \leq y2 \leq 1$ , and  $0 \leq x2 + y2 \leq 1$  and being formed between said n-layer and said p-layer; and

a metal electrode formed on said p-layer,

## characterized in that

said p-layer has at least a double layer structure having a first p-layer satisfying the formula  $\text{Al}_{x4}\text{Ga}_{y4}\text{In}_{1-x4-y4}\text{N}$ , where  $0 \leq x4 \leq 1$ ,  $0 \leq y4 \leq 1$ , and  $0 \leq x4 + y4 \leq 1$  and a second p-layer satisfying the formula  $\text{Al}_{x5}\text{Ga}_{y5}\text{In}_{1-x5-y5}\text{N}$ , where  $0 \leq x5 \leq 1$ ,  $0 \leq y5 \leq 1$ , and  $0 \leq x5 + y5 \leq 1$ , wherein said second p-layer is formed on said first p-layer in direct contact with said metal electrode and is doped with an acceptor impurity in concentration nearly equal to an impurity concentration taking minimum driving voltage of said device.

2. A light-emitting semiconductor device according to claim 1, wherein said second p-layer is doped with an acceptor impurity in concentration more heavily than an impurity concentration taking maximum hole concentration.

3. A light-emitting semiconductor device according to claim 1, wherein said first p-layer is doped with an acceptor impurity in concentration nearly equal to an impurity concentration taking maximum hole concentration.

4. A light-emitting semiconductor device according to

- claim 1, wherein concentration of said acceptor impurity doped into said first p-layer is lower than an arbitrary middle concentration A between concentration taking maximum hole concentration and concentration taking minimum driving voltage of said device and concentration of said acceptor impurity doped into said second p-layer is said arbitrary middle concentration A or higher. 5
5. A light-emitting semiconductor device according to claim 4, wherein said acceptor impurity doped into said first and second p-layers is magnesium (Mg). 10
6. A light-emitting semiconductor device according to claim 5, wherein said arbitrary middle concentration A is  $1 \times 10^{20}/\text{cm}^3$ . 15
7. A light-emitting semiconductor device according to claim 5, wherein Mg concentration doped into said first p-layer is in the range of  $1 \times 10^{19}/\text{cm}^3$  to said arbitrary middle concentration A and Mg concentration doped into said second p-layer is in the range of said arbitrary middle concentration A to  $1 \times 10^{21}/\text{cm}^3$ . 20
8. A light-emitting semiconductor device according to claim 5, wherein Mg concentration doped into said first p-layer is in the range of  $1 \times 10^{19}/\text{cm}^3$  to  $1 \times 10^{20}/\text{cm}^3$  and Mg concentration doped into said second p-layer is in the range of  $1 \times 10^{20}/\text{cm}^3$  to  $1 \times 10^{21}/\text{cm}^3$ . 25
9. A light-emitting semiconductor device according to claim 1, wherein said acceptor impurity doped into said first p-layer is magnesium (Mg) and wherein said impurity concentration taking maximum hole concentration is in the range from  $1 \times 10^{19}/\text{cm}^3$  to  $5 \times 10^{20}/\text{cm}^3$ . 30
10. A light-emitting semiconductor device according to claim 1, wherein said acceptor impurity doped into said second p-layer is magnesium (Mg) and wherein said impurity concentration taking minimum driving voltage is in the range of  $1 \times 10^{20}/\text{cm}^3$  to  $1 \times 10^{21}/\text{cm}^3$ . 35
11. A light-emitting semiconductor device according to claim 1, wherein said acceptor impurity doped into said second p-layer is magnesium (Mg) and wherein said impurity concentration taking minimum driving voltage is  $2 \times 10^{20}/\text{cm}^3$ . 40
12. A light-emitting semiconductor device according to claim 2, wherein said acceptor impurity doped into said second p-layer is magnesium (Mg) and wherein said impurity concentration taking maximum hole concentration is  $5 \times 10^{19}/\text{cm}^3$ . 45
13. A light-emitting semiconductor device according to claim 3, wherein said acceptor impurity doped into said first p-layer is magnesium (Mg) and wherein said impurity concentration taking maximum hole concentration is  $5 \times 10^{19}/\text{cm}^3$ . 50
14. A light-emitting semiconductor device according to claim 1, wherein said second p-layer is gallium nitride (GaN). 55
15. A light-emitting semiconductor device according to claim 1, wherein a third p-layer satisfying the formula  $\text{Al}_x\text{Ga}_y\text{In}_{1-x-y}\text{N}$ , where  $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ , and  $0 \leq x+y \leq 1$  is formed between said emission layer and said first p-layer.
16. A light-emitting semiconductor device according to claim 15, wherein said first p-layer is  $\text{Ga}_{y4}\text{In}_{1-y4}\text{N}$  and said second p-layer is  $\text{Ga}_{y5}\text{In}_{1-y5}\text{N}$ .
17. A light-emitting semiconductor device according to claim 15, wherein said third p-layer is  $\text{Al}_x\text{Ga}_{1-x}\text{N}$ .
18. A light-emitting semiconductor device according to claim 1, wherein said metal electrode is made of one of nickel (Ni) and an alloy including Ni.



FIG. 1

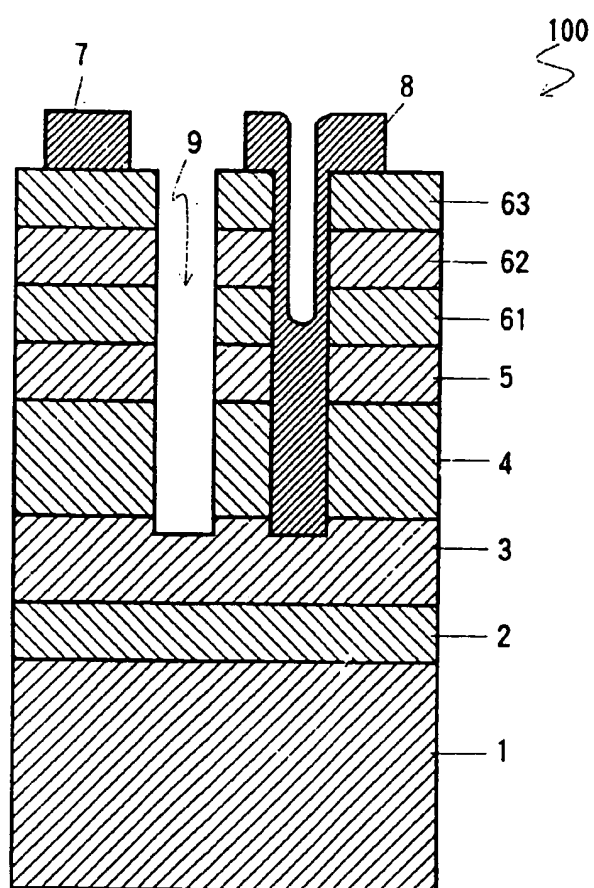


FIG. 2

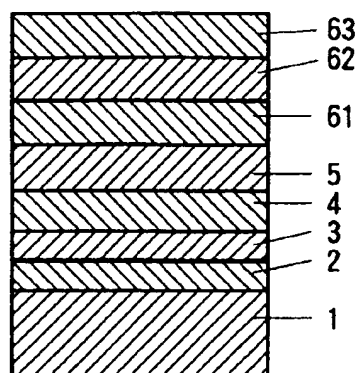


FIG. 3

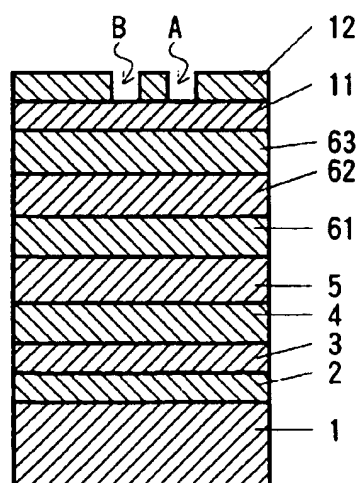


FIG. 4

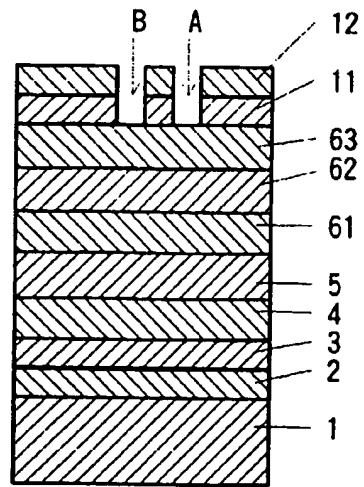


FIG. 5

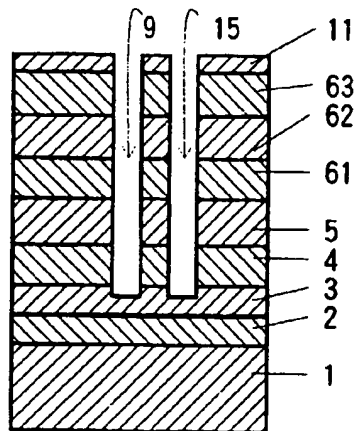


FIG. 6

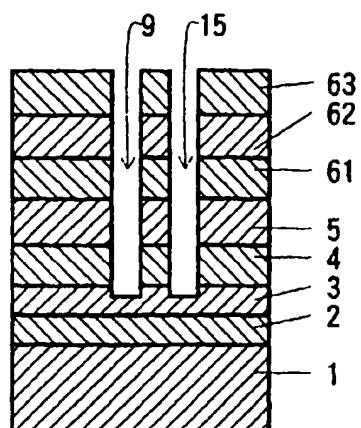


FIG. 7

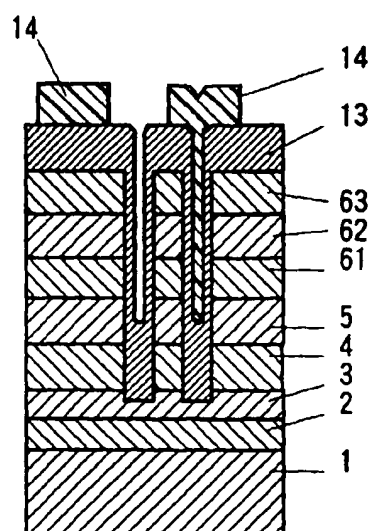


FIG. 8

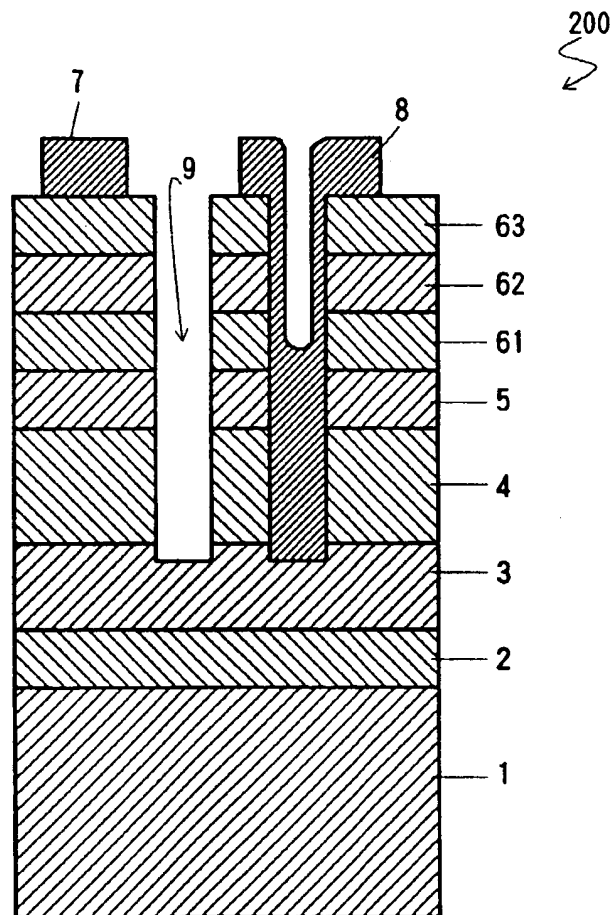


FIG. 9

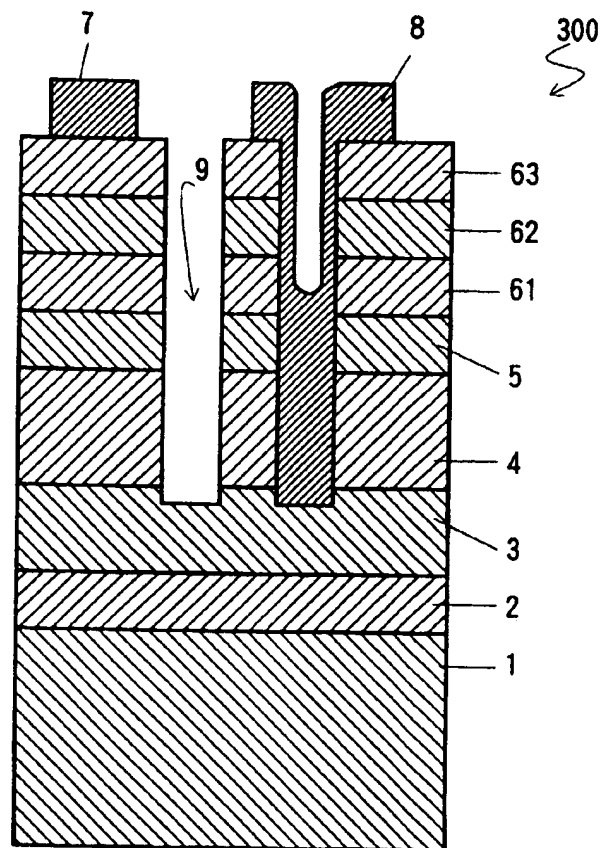


FIG. 10

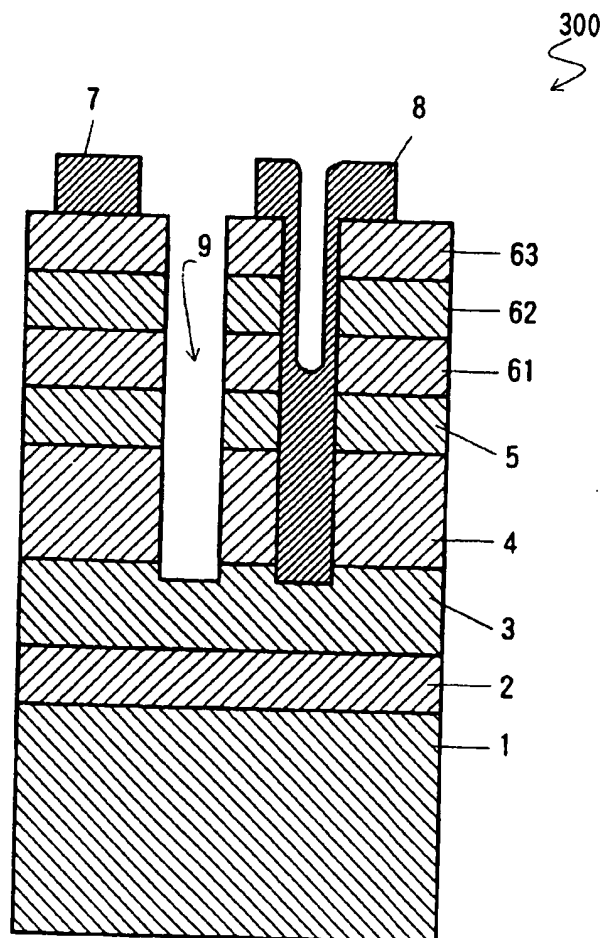


FIG. 11

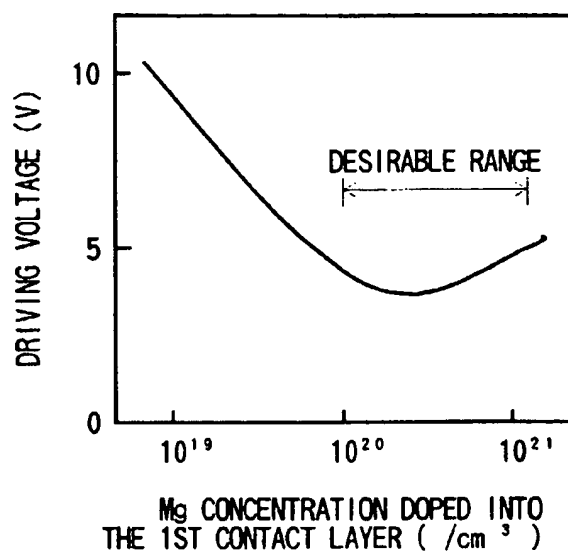


FIG. 12

